

Amendments to the Specification

The paragraph starting at page 1, line 26 and ending at page 2, line 10 has been amended as follows.

--An ink jet printing method has various advantages such as a low noise level, a low running cost, the possibility of high-speed printing, easy compactization of the apparatus, easy color image formation etc., and is therefore widely employed in a printer, a copying apparatus etc. In such a printer or the like, ink to be employed is selected in consideration of printing ~~characteristics~~ characteristics, such as an ejection property and a fixing property, and a print ~~quality~~ quality, such as bleeding in the printed image, optical reflective density, and color developing property.--

The paragraph starting at page 2, line 11 and ending at line 18 has been amended as follows.

--It is well known that the ink is divided, in terms of a colorant contained therein, into two ~~categories of~~ categories: a dye based ink and a pigment based ink. Among these, the pigment ink containing a water-insoluble colorant has advantages such as superiority in water resistance and light fastness, and sharp character quality in comparison with the dye ink containing a water-soluble colorant.--

The paragraph starting at page 2, line 19 and ending at page 3, line 17 has been amended as follows.

--As an example of pigment ink to be employed in the ink jet recording, a pigment ink utilizing a dispersant is known. For example, Japanese Patent Application Laid-open No. 5-179183 (~~patent reference 1~~) (JPA 5-179183) discloses a pigment ink utilizing, as a pigment dispersant, a block polymer of the so-called AB, or BAB type. Also Japanese Patent Application Laid-open No. 7-53841 (~~patent reference 7~~) (JPA 7-53841) discloses a pigment ink utilizing a triblock polymer of the ABC type as a dispersant. For improving the fixing speed of a pigment dispersed by a dispersant of such type and increasing the optical density and the water resistance thereof, ~~the patent reference 7~~ JPA 7-53841 is known to disclose, as essential conditions, two solvents constituted of a polyol/alkylene oxide condensate and a cyclic amide derivative such as 2-pyrrolidone for dissolving the same. ~~This patent reference 7~~ JPA 7-53841 recognizes that a drying fixation speed of the ink and a solvent evaporation from the nozzle or a clogging therein are mutually contradictory factors, and, discloses an invention for improving the fixation speed of the pigment utilizing a dispersant, in comparison with a comparative example employing a cyclic amide derivative alone such as 2-pyrrolidone. ~~This patent reference 7~~ JPA 7-53841 does not describe at all an ink jet head to be used.--

The paragraph starting at page 3, line 18 and ending at page 4, line 2 has been amended as follows.

--Also there is known a pigment ink employing a self-dispersible pigment, without utilizing a dispersant such as the aforementioned block polymer. For example, WO 96/18695 (~~patent reference 3~~) and WO 96/18696 (~~patent reference 4~~) disclose a pigment utilizing carbon black on which a hydrophilic group is directly bonded to the surface. Such pigment ink aggregates without penetrating into a printing medium (recording medium) in an image dot formation. As a result, the colorant (pigment) becomes unevenly distributed in the vicinity of the surface of the printing medium.--

The paragraph starting at page 4, line 3 and ending at page 6, line 5 has been amended as follows.

--An image formed by a pigment ink, observed in a single dot, has a uniform density distribution, and is considered acceptable in its outer shape. However, in the ink jet recording, the dot diameter of the pigment ink does not spread much. Therefore, a further improvement in the pigment is desirable in order to obtain a larger area factor in the ink jet recording. Also in the conventional pigment ink, in case a printing medium on which such pigment ink is applied has an insufficient ink absorbing property, the pigment aggregates on the surface of such a medium, thereby resulting in an image deficient in the uniformity of the colorant fixation. Also not only does a pigment ink in which the aforementioned aggregation reaction is relatively strong cause an uneven aggregation as in the conventional pigment ink, but also it may generate a colorant-lacking portion of a "crack" shape in the pigment fixed on the printing medium. Such a "crack" has a relatively large size that is noticeable also by the bare eyes, so that such a "crack" itself deteriorates

the print quality. Also such crack portion exposes the background of the printing medium, thereby resulting in a decrease in the overall optical density. Such a “crack” often appears on a printing medium bearing a coated layer (resin layer) for accepting the ink, such as a transparency film. This is because the aggregation of the pigment is influenced by a substance contained in the resin layer. Particularly, in the case where the resin layer contains a cationic substance, an ink of an anionic pigment shows a rapid aggregation. The Basically, the aforementioned aggregation-related issues appear conspicuously basically in the case where a pigment ink alone is used for printing, but are found to occur also in an ink utilizing a dye and a pigment as colorants and requiring a dispersant for such pigment, as disclosed in Japanese Patent Application Laid-open No. 2-276873 (~~patent reference 5~~) (JPA 2-276873). For resolving such a “crack” problem, Japanese Patent Application Laid-open No. 11-240145 (~~patent reference 6~~) (JPA 11-240145) discloses an invention based on a combination of a self-dispersible pigment and a dye. Also US Laid-Open No. 2003/0024434 Laid-open (~~patent reference 8~~) (US 2003/0024434) discloses an ink utilizing a combination of a special self-dispersible pigment, a dye and plural solvents (a humectant and a penetrant) thereby satisfying high-speed fixation and optical density. ~~This patent reference 8~~ US 2003/0024434 discloses, as an only example utilizing a printer of a trade name Lexmark Z51 (black ejection amount of 27 picoliters), a combination of self-dispersible pigment:dye = 1:1 and 7.5 mass% of 2-pyrrolidone. US 2003/0024434 ~~The patent reference 8~~ suggests a range of pigment:dye from 0.75:1 to 2.5:1, but such disclosure is limited to a range where the optical density is considered satisfactory. Also it discloses a permissible range of 2-pyrrolidone of 3 to 10 mass%, but no basis therefor is disclosed.--

The paragraph starting at page 6, line 6 and ending at page 7, line 13 has been amended as follows.

--For the ink to be used in the ink jet recording method, it is important, in addition to the properties relating to the image quality, to secure stable ink ejection even in the case of intermittent ejections. In case an ink jet printing head having a plurality of nozzles ~~gets in pause~~ is paused and is exposed to the air, there results evaporation of water or a solvent in the vicinity of the ejection orifice, depending upon a non-ejection time including a difference in the ejection history of each nozzle, whereby a normal printing operation cannot be executed in certain nozzles. Thus the ink is not ejected uniformly from the nozzles, thus generating a defect on the image or causing a deflection in the ejecting direction, thereby deteriorating the print quality. For this reason, in the conventional ink jet head, there is executed an ejection not for recording (such ejection being called a preliminary ejection) even by interrupting a recording operation, in order to apply a safety factor on a non-ejection time inducing such ejection failure, thereby securing the reliability of the head. Since such preliminary ejection often interrupts the recording operation, it is proposed, in order to shorten the time of suspension as far as possible, to provide ink receiving portions on both ends outside a recording area and to execute the preliminary ejection in a closer ink receiving portion depending on the position of the scanning head (for example Japanese Patent Application Laid-open No. 8-118674 (~~patent reference 9~~)) (JPA 8-118674), or to execute the preliminary ejection on an end portion of a paper constituting the recording medium (for example Japanese Patent Application Laid-open No. 7-314708 (~~patent reference 10~~)) (JPA 7-314708).--

The paragraph starting at page 8, line 16 and ending at page 9, line 10 has been amended as follows.

--The present invention has recognized, as a new target, the provision of an ink capable of improving (extending) a maximum elapsed time, or a first-ejection time, from the end of ejection by the ink jet ejection unit to a time when a next ejection can still be executed normally, and has been made as a result of intensive investigations on an ink containing a self-dispersible pigment and a dye. In the course of such investigations, the present inventors have acquired knowledge that an ink droplet, ejected from a nozzle after a pause for a certain time, even if properly ejected, may result in a decrease in the density of an image formed by such an initial ink droplet, or may result in a deterioration of the image quality by a decrease in the image density when an entire image is formed. In an investigation with a variation in the ink composition (particularly ~~an~~ a pigment: dye ratio and 2-pyrrolidone content in the ink) and the ink temperature (particularly at the normal temperature and at a high temperature), it is found that such a phenomenon is also influenced by these parameters.--

The paragraph starting at page 11, line 13 and ending at page 12, line 4 has been amended as follows.

The aforementioned invention ~~allows to prevent~~ helps prevent a decrease in the optical image density by a first ink droplet immediately after a first-ejection time, and is capable of improving the first-ejection time, that has not been improved in the prior

technology, to at least 1.5 times of the prior technology, while satisfying the optical image density (hereinafter represented as OD) of the entire image, thereby improving the reliability of the ink. As a result, a high-quality printing can be achieved without an image defect or an ejection failure, thus providing a high-quality image with an excellent throughput. Particularly, in the case of since an ink jet head with an ejection amount of 10 picoliters or less, there is a tendency that a first-ejection time becomes n seconds when an ejection amount is n picoliters. Therefor the ink of the present invention is extremely effective in the case of forming a high-quality image at a high speed and with a small liquid droplet.--

The paragraph starting at page 14, line 4 and ending at line 25 has been amended as follows.

--The present inventors have investigated the first-ejection property when the ink is in a normal temperature and when the ink is regulated at a high temperature, by varying the ratio of a pigment and a dye in the aforementioned colorants in the ink and the mass% content of 2-pyrrolidone in the ink and assuming various printing environments. The aforementioned “normal temperature” of the ink means from 15 to 35°C, and the “high temperature”, assuming a temperature regulation, means a temperature higher than the normal temperature, ~~and, in~~ temperature. In the present invention, the temperature regulation is performed based on a temperature setting of from 40 to 50°C. ~~Also~~ Also, the aforementioned first-ejection property is defined by “time of suspension (also called a suspension time) of ink ejection from a certain nozzle of an ink jet recording head, after

which time the ink can still be normally ejected from such nozzle”, and the first-ejection property is satisfactory (improved) in the case where the ink is re-ejected normally after a longer suspension of the ink ejection.--

The paragraph starting at page 14, line 26 and ending at page 15, line 18 has been amended as follows.

--For a specific evaluation, after ink of a predetermined amount is ejected from all nozzles, the ink ejection is suspended for a predetermined time. Then a first ejection state, when the ink is again ejected from all the nozzles, is evaluated, and the following cases 1), 2) and 3) are regarded as unacceptable while other cases are regarded as a normal ejection, and a longest time capable of normal ejection among the aforementioned suspension times is defined as the first-ejection time of the ink:

- 1) no ejection;
- 2) ejection is possible, but the dot density is lower than that in an acceptable range for an image (density is about 50% or less) in comparison with an ejection state without a suspension time;
- 3) ejection is possible, but the dot impact position deviates outside an acceptable range for an image (positional deviation in excess of 1 pixel) in comparison with an ejection state without a suspension time.--

The paragraph starting at page 16, line 13 and ending at page 17, line 5 has been amended as follows.

--Then, Figs. 2A and 2B show a schematic relationship between the amount of 2-pyrrolidone and the first-ejection property. Fig. 2A shows a case where the ink is at the normal temperature, and Fig. 2B shows a case where the ink is at a high temperature. In Fig. 2B, the result of evaluation is also indicated with an error bar, in consideration of a fluctuation in the temperature control. In either environment, the first-ejection property is rapidly improved in the case where the amount of 2-pyrrolidone reaches 12 mass% or higher. However, as shown in Figs. 1A and 1B, the characteristics vary depending on the temperature environment when the content increases. At the normal temperature, the first-ejection property becomes sufficiently satisfactory at a content of 15 mass% or higher, but the first-ejection time tends to become shorter. On the other hand, at the high temperature, the first-ejection time tends to become longer approximately in proportion to the content of 2-pyrrolidone until it reaches 27 mass%.--

The paragraph starting at page 17, line 14 and ending at line 20 has been amended as follows.

--Also the results in Figs. 1A and 1B indicate that a sufficient first-ejection property may not be obtained even with a content of 2-pyrrolidone of 12 mass% or higher, in the case where the colorant is constituted of ~~the~~ pigment only. Thus, the pigment-dye ratio and the amount of 2-pyrrolidone are both important factors for the first-ejection property.--

The paragraph starting at page 17, line 21 and ending at line 27 has been amended as follows.

--It is also clarified that an effect on the first-ejection property can be obtained by regulating the ink at a certain temperature range according to the solvent composition of the ink. The temperature regulation also provides another effect of providing the same ejection characteristics in any ~~environments~~, environment, thereby providing a constant image quality.--

The paragraph starting at page 20, line 14 and ending at line 25 has been amended as follows.

--Examples of the anionic group bonded to carbon black include -COOM, -SO₃M, -PO₃HM, -PO₃M₂, -SO₂NH₂, and -SO₂NHCOR (wherein M represents a hydrogen atom, an alkali metal, ammonium or an organic ammonium group, and R represents a linear or branched alkyl group with 1 to 12 carbon atoms, a substituted or non-substituted phenyl group or a substituted or non-substituted naphthyl group). In the case where R represents a phenyl group with a substituent or a naphthyl group with a substituent, such substituent of the phenyl or naphthyl group can be, for example, a linear or branched alkyl group with 1 to 6 carbon atoms.--

The paragraph starting at page 20, line 26 and ending at page 21, line 5 has been amended as follows.

--The ~~alkali~~ alkali metal for can be for example lithium, sodium or potassium, and the organic ammonium for "M" can be for example mono- to tri-methylammonium, mono- to tri-ethylammonium, or mono- to tri-methanol ammonium. Among these anionic groups, -COOM or -SO₃M is preferred because of a large effect for stabilizing the dispersion state of carbon black.--

The paragraph starting at page 22, line 19 and ending at page 23, line 4 has been amended as follows.

--As an anionic dye to be employed in the present embodiment, an acidic dye, a direct dye or a reactive dye known in the ~~art~~ art can be advantageously employed. Particularly preferably, the dye has a skeleton of a disazo or trisazo structure. It is also preferable to employ two or more dyes of different skeletal structures. For example, in the case of preparing a black ink, it is possible to use dyes other than black dye, such as those of cyan, magenta, yellow etc. within such an extent that the color is not changed significantly. The aforementioned self-dispersible carbon black can be employed as a black pigment, and as a colorant in a black ink.--

The paragraph starting at page 24, line 25 and ending at page 25, line 17 has been amended as follows.

--The ink of the present invention can be prepared with a desired color by selection of the colorant. In the case of forming a multi-color image, there ~~are~~ is employed

a set of a cyan ink, a magenta ink and a yellow ink, or a set of a cyan ink, a magenta ink, a yellow ink and a black ink, and it is preferred that at least one of the inks constituting such ink set is an ink of the present invention. Particularly in an ink set including a black ink, at least the black ink is preferably formed by the ink of the present invention, since it can improve the OD of characters. Also in case of forming a multi-color image, other color inks to be employed with such black ink (for example yellow, cyan or magenta ink or a pale colored ink thereof) can be dye based inks of a relatively high penetrating speed, commonly employed in the ink jet recording of a multi-color image. Examples of compositions of such inks are shown in the following, wherein the total amount of the ink is set to 100 parts:--

The paragraph starting at page 27, line 2 and ending at page 28, line 9 has been amended as follows.

--Also an ink container, such as an ink cartridge containing the ink of the embodiment or a recording head integrating an ink containing part and an ink ejecting means and so constructed as to be detachably mounted on an ink jet printer, is also included in an embodiment of the present invention. Further, an ink set in which a black ink of the present embodiment containing the aforementioned self-dispersible carbon black as the colorant and other color inks are contained in respectively independent containers, is also included in an embodiment of the present invention. The printing medium to be used in the present embodiment is not particularly limited and can be, for example, paper, non-woven cloth, OHP sheets or leather. A specific example of the recording medium is a

printing medium provided with a coated layer. The coated layer contains a water-soluble polymer or a water-dispersible polymer, and such water-soluble polymer can be, for example, at least one resin selected from polyvinyl alcohol, anion-modified polyvinyl alcohol, cation-modified polyvinyl alcohol, acetal-modified polyvinyl alcohol, aqueous polyurethane, polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymer, vinylpyrrolidone-dimethylaminoethyl methacrylic acid copolymer, quaternalized vinylpyrrolidone-dimethylaminoethyl methacrylic acid copolymer, vinylpyrrolidone-methacrylamidepropyl chlorotrimethyl ammonium copolymer, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, cationized hydroxyethyl cellulose polyester, polyacrylic acid, polyacrylate ester, melamine resin, a graft copolymer containing polyester and polyurethane, albumin, gelatin, casein, starch, cationized starch, gum ~~Arabic~~ arabic and sodium alginate.--